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THE ACTION OF TRIETHYLPHOSPHITE AND SODIUM DIETHYLPHOSPHITE
 ON CERTAIN DIHALOGEN DERIVATIVES

B. A. Arbuzov, B. P. Lugovkin
 Chem Inst imeni A. M. Butlerov,
 Kazan State U imeni V. I. Ul'yanov-Lenin

[Phosphonic esters prepared by reactions of the type described in this paper can be converted into halophosphonates, i.e., compounds of a class several representatives of which are known to possess cholinesterase inhibitor activity. It is not known whether or not the Soviet investigators were actually interested in the synthesis of halophosphonates exhibiting this type of activity and whether the phosphonic esters described by them form the most suitable intermediates for the conversion in question; this merely indicates a potential application of results obtained in research along the lines mentioned in the article].

A. Ye. Arbuzov showed that completely esterified phosphorous acid under the influence of alkyl halides is isomerized into esters of alkylphosphonic acids (1). Later, he extended this reaction to include dihalogen derivatives of paraffins. Thus A. Ye. Arbuzov and N. P. Kushkova (2) obtained the ethyl ester of iodomethylphosphonic acid by the action of triethylphosphite on methylene iodide, although they did not succeed in substituting a phosphonic radical for the second iodine atom. Nylen (3), reacting two molecules of sodium diethylphosphite with trimethylene bromide, obtained the normal reaction product -- the ester of trimethylenediphosphonic acid. This reaction was repeated by A. Ye. Arbuzov and N. P. Kushkova (2). Nylen (3) in the reaction of sodium diethylphosphite with ethylene bromide obtained ethylene. L. N. Parfent'yev and M. Shafiyev (4) reacted triethylphosphite with trimethylene, obtaining γ -bromopropylphosphonic ester. Later, G. Kosolapoff (5) reacted triethylphosphite with ethylene bromide, but did not obtain the corresponding esters of β -bromoethylphosphonic acid or the ester of ethanediphosphonic acid. On the contrary, as the experiments of Kosolapoff (6) showed, when triethylphosphite reacts with trimethylene bromide it is possible to substitute either one or two bromine atoms with phosphonic groups.

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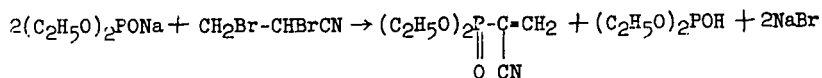
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In 1947 Ford-Moore and Williams (7) showed that when triethylphosphite reacts with methylene iodide, the tetraethyl ester of methane diphosphonic acid can easily be obtained. But when triethylphosphite was reacted with propylene bromide, Ford-Moore and Williams did not obtain the expected ester of β -bromopropylphosphonic acid, but a small quantity of the ester of propenylphosphonic acid which was formed by the splitting off from the ester of hydrogen bromide. The formation of the β -bromoethylphosphonic ester by the action of triethylphosphite on ethylene bromide was confirmed by Kosolapoff (8).

As the survey data in literature shows, reactions between complete esters of phosphorous acid or sodium diethylphosphite and dihalogen derivatives of saturated hydrocarbons proceed differently when the halides are differently grouped. The unusual behavior of dihalogen derivatives of paraffins in the above reactions spurred us to extend the experiments to other dihalogen derivatives.

We studied the interaction of sodium diethylphosphite with α,β -dibromopropionitrile. An investigation of the reaction products showed that the reaction proceeds with the formation of the ethyl ester of the nitrile of phosphonoacrylic acid and diethylphosphorous acid. Apparently the primary reaction product splits off a hydrogen bromide which with sodium diethylphosphite forms free diethylphosphorous acid:



(Another possible constitution for the ester obtained is $(\text{C}_2\text{H}_5\text{O})_2\text{P}-\underset{\text{O}}{\text{C}}=\text{CH}-\text{CH}-\text{CN}$).

The acid in its pure form could not be isolated after saponification of the ester. Thus, the reaction we studied proceeds along the lines of the reaction of propylene bromide with triethylphosphite which was studied by Ford-Moore and Williams.

It should be noted that according to our findings the reaction between β -chloropropionitrile and sodium diethylphosphite proceeds normally and the ethyl ester of the nitrile of β -phosphonopropionic acid $(\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{CH}_2\text{CH}_2\text{CN}$ is obtained with a satisfactory yield. On saponification of the nitrile ester, β -phosphonopropionic acid with bp 166° (9) was obtained.

The interaction of sodium diethylphosphite with styrene dibromide proceeded quite differently. By analogy with α,β -dibromopropionitrile, one might in this case expect formation of the ester of styrylphosphonic acid. However, as the experiment showed, the principal product of this reaction was styrene, yielded in the amount of 53.7%. After the distillation of the complex mixture of phosphorus-containing fractions, the presence in them of the ester of hypophosphoric acid was proved by the fact that with β -naphthylamine the β -naphthylamide of the diethyl ester of phosphoric acid with mp of 69° (mixed sample) was formed. Thus, as in the case of dibromoethane which Nylen (3) observed, sodium diethylphosphite in this reaction behaves like dissolved sodium, removing the halogen from styrene dibromide. The phosphonic residue which is formed undergoes complex conversions and yields a mixture of products, chief among which is tetraethyl hypophosphate, as was earlier observed by A. Ye. Arbuzov and B. A. Arbuzov (10) in the case of the action of bromine on sodium diethylphosphite.

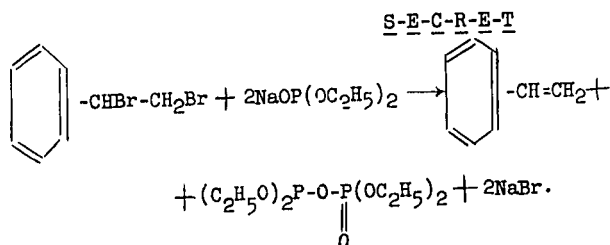
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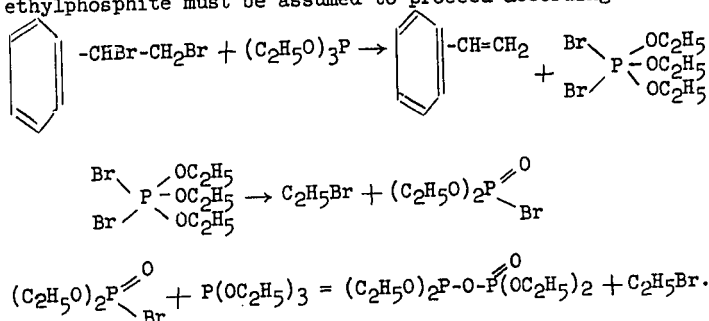
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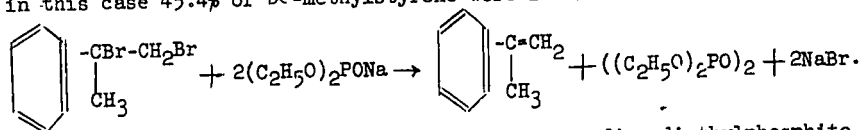


It is extremely interesting that the action of styrene dibromide on triethylphosphite leads to a like result. When these were reacted at 155-160°, ethyl bromide was formed. From the reaction products were separated styrene to the amount of 50.2% (of the styrene dibromide entering into the reaction), a small quantity of diethylphosphorous acid, and a complex mixture of organophosphorus derivatives in which the ester of hypophosphoric acid was proved present by the formation of the β -naphthylamide of the diethyl ester of phosphoric acid (mp 69°) when the mixture was reacted with β -naphthylamine (11). Thus, the interaction of styrene dibromide with triethylphosphite must be assumed to proceed according to the scheme:

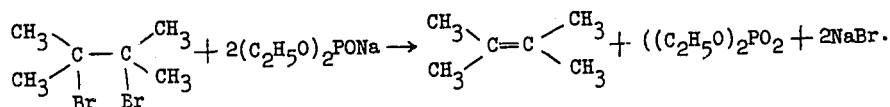


Such a course of the reaction is fully possible, since Hall and Jacobson (12) have described the formation of tetraethylpyrophosphate by the action of the chloride of diethylphosphoric acid on triethylphosphate. The formation of small quantities of diethylphosphorous acid is explained by the partial splitting off of hydrogen bromide from the dibromostyrene under the conditions of the reaction. A special experiment showed that at 155-170° dibromostyrene liberates hydrogen bromide, hydrogen bromide reacting with triethylphosphorous acid and ethyl bromide.

The reaction of sodium diethylphosphite with α -methylstyrene dibromide proceeds similarly to that with styrene dibromide. From the reaction products in this case 45.4% of α -methylstyrene were isolated:



It can also be added that in the case when sodium diethylphosphite acts on tetramethylethylene dibromide, tetramethylethylene is formed with a good yield (the reaction was studied by N. P. Bogonostseva):

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EXPERIMENTAL PART

Action of β -Chloropropionitrile on Sodium Diethylphosphite -- To an ether solution of sodium diethylphosphite -- prepared from 44.2 g diethylphosphorous acid (theoretically 43.9 g) and 7.2 g metallic sodium in 450 ml dry ether -- were added drop by drop 28.5 g β -chloropropionitrile (bp 63-65° at 10 mm; n_D^{20} 1.4370; d_4^{20} 1.1461) (14) during 30 minutes. Sodium chloride was precipitated. The ether solution was boiled for an hour on a water bath. The sodium chloride was filtered off and washed with ether; 17 g of it were obtained, as against the theoretical yield of 18.3 g. The ether was distilled off and the residue distilled in a vacuum. After a second vacuum distillation there was separated the ethyl ester of β -phosphonopropionitrile (bp 150-152° at 7 mm) as a colorless liquid, soluble in water, n_D^{20} 1.4380, in a quantity of 42.7 g (70.2%). For analysis the substance was again distilled at 2 mm, bp 127-128°.

n_D^{20} 1.4380; d_4^{20} 1.1127

0.0980 g of substance; 27.04 ml NaOH ($T = 0.02154$). Found: P 16.46%.

Calculated for $C_7H_{14}O_3NP$: P 16.23%.

Saponification -- 9.9 g of the substance were heated with 30 ml dilute hydrochloric acid (2:1) in a sealed tube at 115-130° for 8 hours. After repeated evaporation (on a water bath) a solid, colorless residue was obtained. β -Phosphonopropionic acid was extracted by a Soxhlet apparatus with dry benzene, and then with dry acetone. After the solvents had been distilled off, 6.2 g (78.5%) of acid with mp of 166° were obtained; a mixed sample melted at the same temperature.

Action of α, β -Dibromopropionitrile on Sodium Diethylphosphite -- To an ether solution of sodium diethylphosphite (53.3 g diethylphosphorous acid, as against 52.6 g by theory, and 8.7 g metallic sodium in 500 ml dry ether) were added drop by drop during 30 minutes 40.6 g α, β -dibromopropionitrile (bp 89-90° at 10 mm; n_D^{20} 1.5390; d_4^{20} 1.20995) (15) in 40 ml dry ether. After appropriate treatment there were obtained 30.3 g (78.7%) of anhydrous sodium bromide, as against the theoretical 38.9 g.

After repeated vacuum distillation the following were isolated: (a) diethylphosphorous acid with bp of 115-120° at 7 mm, n_D^{20} 1.4080, d_4^{20} 1.0667, with a yield of 7 g (11.9%); (b) the ethyl ester of the acid of phosphonoacrylic acid with bp of 124-127° at 1 mm, n_D^{20} 1.4380, d_4^{20} 1.1127, as an oily liquid easily soluble in water and having an immediate decolorizing action on bromine water and potassium permanganate. The yield was 9.5 g (26.4%).

0.0847 g of the substance: 24.13 ml NaOH ($T = 0.02148$). Found: P 16.94%.

Calculated for $C_7H_{12}O_3NP$: P 16.40%.

Saponification -- 6.4 g of the substance were heated with 30 ml dilute hydrochloric acid (1:1) in a sealed tube at 150-165° for 10 hours. After repeated evaporation until the HCl was completely eliminated, 5.3 g of a solid substance contaminated with a viscous liquid was obtained. After extraction with alcohol (dehydrated by CaO) 5.2 g (29%) ammonium chloride were separated, and removal of the alcohol left 4 g of a viscous liquid containing insignificant

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quantities of a crystalline product. By treatment of this mixture with barium carbonate and heating it, a mixture of barium salts was obtained. Fractional recrystallization from water yielded 0.6 g of a barium salt insoluble in water. By analysis the salt corresponds to either the barium salt of phosphonoacrylic acid ($C_6H_4P_2O_{11}Ba_3$) or barium phosphate ($BaHPO_4$).

0.4388 g of Ba salt (after drying in revolving desiccator at 100° to a constant weight: 0.4312 g $BaSO_4$. Found: Ba 0.2538g. Calculated: for $C_6H_4P_2O_{10}Ba_3$, Ba 0.2547 g; for $BaHPO_4$, Ba 0.2581 g.

A soluble barium salt was separated in large quantities up to 3.2 g [sic]. From the determination of barium, this salt approaches the formula $C_6H_8O_{10}P_2Ba$.

0.7342 g of Ba salt (after drying in a revolving desiccator at 100° to a constant weight): 0.4324 g $BaSO_4$. Found: Ba 0.2545 g. Calculated for $C_6H_8O_{10}P_2Ba$: Ba 0.2295 g.

Action of α, β -Dibromopropionitrile on Triethylphosphite -- To 20.2 g dibromopropionitrile were added drop by drop 32.8 g triethylphosphite (theoretically 31.5 g) during 30 minutes. The temperature in the reaction mixture rose from 16° to 87° and was held within the limits $87-99^\circ$, while ethyl bromide was distilled off. At the end of the reaction the contents were heated for 15 minutes up to 150° ; 19 g ethyl bromide (20.6 g by theory) with bp of $38-40^\circ$ were obtained. The yield was 92.2%. No individual products could be isolated, even by means of a series of vacuum distillations.

Action of ω -Bromostyrene on Sodium Diethylphosphite -- Into a toluene solution of sodium diethylphosphite (13.1 g diethylphosphorous acid -- as against 12.1 g by theory -- and 2 g metallic sodium in 10 ml dry toluene) were poured 16.1 g ω -bromostyrene (bp $88-90^\circ$ at 10 mm; n_D^{20} 1.6018; d_4^{20} 1.4094). No sodium bromide was precipitated in this case or in an ethyl ether solution. It was, however, precipitated in boiling toluene. In this solvent, heating was carried out for 4 hours. After appropriate treatment 6.6 g (by theory 9 g) of anhydrous sodium bromide were separated. The reaction product was distilled in vacuum first at 10 mm, and the high-boiling part was then distilled at 1 mm. After several distillations and preliminary treatment of the appropriate fraction with water there were separated 7.1 g (44%) of the initial ω -bromostyrene (bp $213-220^\circ$; n_D^{20} 1.5850; d_4^{20} 1.3673). After another distillation the boiling point was $213-215^\circ$, n_D^{20} 1.5938, d_4^{20} 1.3947. In the first vacuum distillation from the high-boiling portion the ethyl ester of diphosphonostyrene (bp 181° at 1 mm; n_D^{20} 1.4920; d_4^{20} 1.1524) was separated in the form of a viscous liquid, soluble in water, in a quantity of 1.9 g. The yield was 12.0% (cf the sodium diethylphosphite used).

0.0730 g of the substance: 22.24 ml NaOH ($T=0.01928$). Found: P 16.27%. Calculated for $C_{16}H_{28}O_6P_2$: P 16.40%.

Saponification--0.8 g of the substance was heated with 10 ml dilute hydrochloric acid (1:1) in a sealed tube at $120-130^\circ$ for 7 hours. The solution was treated with ether, and 0.1 g of an oily liquid was extracted. After repeated evaporation 0.5 g (0.56 g by theory) of diphosphonostyrene was obtained in the form of colorless crystals easily soluble in water and alcohol (mp $212-214^\circ$). After heating of the aqueous solution with animal charcoal and evaporation, an acid with the same melting point was obtained.

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0.514 g of the substance: 21.60 ml NaOH ($T=0.01928$). Found: P 22.43%.
 Calculated for $C_8H_{12}O_6P_2$: P 23.30%.

The ester and acid of diphosphonostyrene require prolonged heating (up to 80 hours) with periodic addition of nitric acid (sp. gr. 1.5). Analysis is conducted after drying in a revolving desiccator at 100°.

Action of ω -Bromostyrene on Triethylphosphite -- To 14.9 g ω -bromostyrene, heated to 200-210°, 14.5 g triethylphosphite were slowly added, drop by drop, during one hour. The mixture was then distilled; 12.7 g triethylphosphite were distilled off. On heating on a water bath (to 80°), no ethyl bromide evolved. The distilled triethylphosphite was poured into the reaction flask. The original substances were distilled in vacuum (10 mm) with an insignificant residue.

Repeat Experiment -- 26.2 g triethylphosphite and 14.5 g ω -bromostyrene were heated in a sealed tube at 180-200° for 8 hours. When the contents were distilled in vacuum (12 mm), the original ω -bromostyrene was recovered along with the ethyl ester of ethylphosphonic acid and an insignificant residue.

Action of Styrene Dibromide ($C_6H_5CHBr-CH_2Br$) on Sodium Diethylphosphite -- To an ether solution of sodium diethylphosphite (37.5 g diethylphosphorous acid, as against 36.1 by theory, and 6 g metallic sodium in 500 ml dry ether) there was added drop by drop during 35 minutes an ether solution of 34.6 g styrene dibromide (mp 72°) in 80 ml dry ether. Sodium bromide was precipitated. Heat was applied for 2 hours so that the ether boiled. After the usual treatment the reaction product was distilled in vacuum (11 mm), the fractions being as follows: fraction I, bp 43-90°, colorless liquid, weight 18.3 g; fraction II, bp 90-132°, colorless liquid, weight 14.4 g, containing colorless crystals. The residue was a viscous liquid containing a crystalline substance. After cooling, 0.8 g of the original dibromide (mp 70°) was separated. The filtrate was combined with fraction II.

Investigation of Fraction I (bp 43-90° at 11 mm) -- To the fraction (18.3 g) were added 50 ml water; the undissolved product with the odor of styrene was treated with bromine in a chloroform solution on cooling. This yielded 16 g styrene dibromide with mp 72-73° (mixed sample 72°), which corresponds to 6.3 g styrene or 53.7% on the basis of the styrene bromide entering into the reaction). The soluble part of the fraction was apparently diethylphosphorous acid.

Investigation of Fraction II (bp 90-132° at 11 mm) -- After repeated vacuum distillations the following were separated: (a) 4 g of the original styrene dibromide (mp 70-71°), i.e., altogether 7.8 g styrene dibromide were separated; 29.8 g (86.1%) entered into the reaction; (b) from the fraction with bp 105-130° at 3 mm (after preliminary separation of initial styrene dibromide under strong cooling) reacting with β -naphthylamine yielded 1.2 g of the β -naphthylamide of diethylphosphoric acid (boiling point of mixed sample 69°), which corresponds to 1.18 g of ethyl ester of hypophosphoric acid or 3.85% (on the basis of the styrene dibromide entering into the reaction). Neither the ethyl ester of ω -phosphonostyrene nor that of diphosphonostyrene was isolated.

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Action of Styrene Dibromide on Triethylphosphite -- To 16 g styrene dibromide, heated to 155-160°, 22 g triethylphosphite (20.1 g by theory) were added drop by drop during one hour while ethyl bromide was distilled off (below 150° this distillation did not take place). Heating was continued at 165-170° for one hour. This yielded 8.6 g ethyl bromide (by theory 11.8 g) with bp 38-40°.

The reaction product was distilled in vacuum and could be fractionated as follows: fraction I (bp 54-74° at 15 mm) was a colorless liquid weighing 13.6 g; fraction II (bp 103-157° at 2 mm) was a colorless liquid weighing 10.3 g; the remainder, 1.7 g, was an amorphous solid product.

Investigation of Fraction I (bp 54-74° at 15 mm) -- By repeated distillation at 11 mm two fractions were separated. (a) Bp 45-65°, weight 4.7 g. A colorless liquid with the odor of styrene. Bromination produced 7.2 g styrene dibromide with mp 71-72° (mixed sample 71°), which corresponds to 28 g styrene, or 50% (of the styrene dibromide entering into the reaction). (b) Bp 69-72°, n_D^{20} 1.4116, d_4^{20} 1.0627, weight 3.8 g. Impure diethylphosphorous acid. The fraction was completely soluble in water. The Beilstein reaction was negative.

Investigation of Fraction II (bp 103-157° at 2 mm) -- Repeated distillation yielded two fractions. (a) Bp up to 117° at 2 mm. From this fraction were separated 1.7 g of original styrene dibromide (mp 71-72°). (b) Bp 117-131° at 2 mm. After preliminary separation of the original styrene dibromide by cooling, the action of β -naphthylamine yielded 0.8 g of the β -naphthylamide of diethylphosphoric acid (mp 69°), and this corresponds to 0.7 g of ethyl ester of hypophosphoric acid, or 4.8% (on the basis of the styrene dibromide entering into the reaction). Neither the ethyl ester of ω -phosphonostyrene nor that of diphosphonostyrene was isolated. When styrene dibromide was heated (in a separate experiment) under the conditions for carrying out the reaction with triethylphosphite (at 155-170°) there was a considerable yield of hydrogen bromide which was explained by the formation of diethylphosphorous acid. No formation of styrene was observed.

Action of Diethylphosphorous Acid on Styrene Dibromide -- To 9.2 g styrene dibromide, heated to 195-205°, 10.2 g diethylphosphorous acid were added drop by drop during 30 minutes while ethyl bromide was distilled off (below 190° C_2H_5Br was not evolved). The heating was continued for one hour at 210-215°, and 4.1 g of ethyl bromide (bp 38-39°) were distilled off. After the ethyl bromide had been distilled off, the residue, 1.5 g by weight and having an odor of styrene, was treated with bromide in chloroform solution; 0.7 g styrene dibromide (mp 70-71°) was separated, which corresponds to 0.27 g or 7.5% of styrene.

Action of α -Methyl- ω -Bromostyrene ($C_6H_5-\overset{\text{CH}_3}{\underset{|}{C}}=CHBr$) on Sodium Diethylphosphite -- To an ether solution of sodium diethylphosphite (16 g diethylphosphorous acid -- 15 g by theory -- and 2.5 g metallic sodium in 200 ml dry ether) were added drop by drop 21.4 g α -methyl- ω -bromostyrene (bp 103-105° at 11 mm; n_D^{20} 1.5680; d_4^{20} 1.3790) (16) in 20 ml dry ether. Sodium bromide was precipitated. Heat sufficient to boil the ether was applied for one hour. After appropriate treatment 8.4 g anhydrous sodium bromide, or 85.7% (on the basis of the α -methyl- ω -bromostyrene entering into the reaction), were obtained.

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After repeated vacuum distillation the following were isolated: (a) 2.1 g of initial α -methyl- ω -bromostyrene (bp 95-98° at 9 mm, n_D^{20} 1.5680); 19.3 g of the bromide entered into the reaction; (b) the ethyl ester of α -methyl- ω -phosphonostyrene (bp 146-149° at 9 mm; n_D^{20} 1.5210; d_4^{20} 1.1094), in the form of an oily liquid, insoluble in water, which immediately decolorizes a chloroform solution of bromine; the yield was 4 g, or 16% (of α -methyl- ω -bromostyrene entering into the reaction).

0.0828 g of the substance: 18.7 ml NaOH ($T = 0.01928$). Found: P 12.06%. Calculated for $C_{13}H_{19}O_3P$: P 12.20%.

Saponification -- 1.4 g of the substance were heated with 12 ml dilute hydrochloric acid (1:1) in a sealed tube at 135-145° for 6 hours and at 145-160° for 4 hours. After evaporation of ethyl chloride, there remained on the surface of the solution an oily layer weighing 0.5 g and representing impure α -methylstyrene. (With an extended boiling point when α -methylstyrene was heated in a sealed tube with dilute hydrochloric acid (1:1) at 120-130° for 10 hours, under the conditions of the experiment with triethylphosphite, similar results were obtained.) After repeated evaporation on a water bath until HCl was completely eliminated, a viscous liquid was obtained (phosphoric acid); when this was acted on by phenylhydrazine in an alcoholic solution, 1.5 g phenylhydrazine phosphate were obtained; after recrystallization the melting point was 155° (a mixed sample melted at the same temperature).

Action of α -Methyl- ω -Bromostyrene on Triethylphosphite -- To 13.6 g methylbromostyrene, heated to 150-160°, were added drop by drop 12.5 g triethylphosphite (theoretically 11.4 g) during 40 minutes, and ethyl bromide was distilled off (below 150° C_2H_5Br was not distilled off). The heating was continued one hour at 165-170°; 2.3 g of ethyl bromide (36.5% of theory) were distilled off. After repeated vacuum distillations the following were separated: (a) 2.1 g original α -methyl- ω -bromostyrene with n_D^{20} 1.5358, d_4^{20} 1.2668, and bp 208-210° (before distillation the appropriate fraction was treated with water); (b) 3.1 diethylphosphorous acid, with bp 65-80° at 10 mm (the dissolved part of the fraction when treated with water; (c) 5 g of the ethyl ester of α -methyl- ω -phosphonostyrene (bp 149-150° at 1.5 mm, n_D^{20} 1.5190, d_4^{20} 1.1009) which is equivalent to 33.5% (of the α -methyl- ω -bromostyrene entering into the reaction).

0.0796 g of the substance: 18.8 ml NaOH ($T = 0.01928$). Found: P 12.61%. Calculated for $C_{13}H_{19}O_3P$: P 12.20%.

Saponification -- 3.3 g of the substance were heated with 20 ml dilute hydrochloric acid (1:1) in a sealed tube at 120-130° for 10 hours. From the top layer after the evaporation of ethyl chloride were obtained 1.7 g of impure α -methylstyrene. After repeated evaporation of the aqueous solution until all HCl was removed, a viscous liquid -- phosphoric acid -- was obtained. Then, 3.7 g phenylhydrazine phosphate were obtained from this by the reaction of phenylhydrazine. After recrystallization from alcohol the melting point was 154-155°; a mixed sample melted at the same temperature.

Action of α -Methylstyrene dibromide ($C_6H_5-\underset{\text{CH}_3}{\text{CBr}}-\text{CH}_2\text{Br}$) on Sodium Diethyl-

phosphite -- To an ether solution diethylphosphite (33 g diethylphosphorous acid -- 30.3 g by theory -- and 5.3 g metallic sodium in 400 ml dry ether) were added drop by drop during one hour 30.6 g of an ether solution of α -methylstyrene dibromide (prepared from 15 g α -methylstyrene -- bp 163°;

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d_4^{20} 0.9098 -- dissolved in 300 ml dry ether, while 17 g bromine were added drop by drop during 1.5 hours and the solution was cooled by snow). Sodium bromide was precipitated. Heat was applied to keep the ether boiling for 2 hours. After repeated vacuum distillations the following were separated: The first fraction, with bp $41-43^\circ$ at 3 mm, was a colorless liquid, weighing 11.3 g, with n_D^{20} 1.4867 and d_4^{20} 0.9750. On treatment with water, 5.9 g (45.4%) of α -methylstyrene (bp $160-162^\circ$, d_4^{20} 0.9201) were obtained. The soluble part of the fraction was apparently diethylphosphorous acid. Individual compounds could not be isolated from the higher fractions.

CONCLUSIONS

1. A study of the action of sodium diethylphosphite and triethylphosphite on certain dibromides has been carried out. It has been shown that the reaction proceeds differently for dibromides of different constitutions.

2. When sodium diethylphosphite was reacted with α, β -dibromopropionitrile, the ethyl ester of the nitrile of phosphonoacrylic acid was obtained.

3. In the cases of styrene dibromide and α -methylstyrene dibromide the action of sodium diethylphosphite leads to the formation of styrene and α -methylstyrene. The reaction between tetramethylethylene dibromide and sodium diethylphosphite takes place in an analogous manner, with tetramethylethylene being produced as a result. Triethylphosphite acts on styrene dibromide much as does sodium diethylphosphite, removing bromine and forming styrene.

4. The interaction of ω -bromostyrene with sodium diethylphosphite takes place in a unique manner, with the addition of a second molecule of sodium diethylphosphite by a double bond and the formation of the tetraethyl ester of diphosphonophenylethane.

In the case of α -methyl- ω -bromostyrene only the ethyl ester of α -methyl- ω -phosphonostyrene was separated by the action of sodium diethylphosphite.

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